

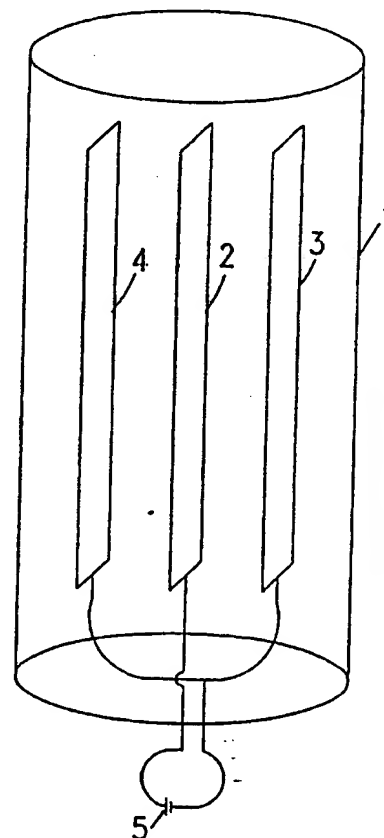


## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup>:</b> <b>C02F 1/46</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/16715</b> <b>(43) International Publication Date:</b> 8 April 1999 (08.04.99)
<b>(21) International Application Number:</b> PCT/IL98/00453 <b>(22) International Filing Date:</b> 17 September 1998 (17.09.98) <b>(30) Priority Data:</b> 121880 1 October 1997 (01.10.97) IL <b>(71) Applicant (for all designated States except US):</b> ARGAD WATER TREATMENT INDUSTRIES LTD. [IL/IL]; P.O. Box 7, 30300 Atlit (IL). <b>(71)(72) Applicant and Inventor:</b> ITZHAK, David [IL/IL]; Rotem Street 32, 84965 Omer (IL). <b>(74) Agents:</b> LUZZATTO, Kfir et al.; Luzzatto & Luzzatto, P.O. Box 5352, 84152 Beer-Sheva (IL).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>With amended claims.</i>

**(54) Title:** WATER TREATMENT METHOD AND DEVICE**(57) Abstract**

A method of treatment of aqueous media comprises applying to the aqueous medium in an electrolytic cell (1) an electrical direct current of a magnitude and at a flow-rate of the liquid in said electrolytic cell such that a combined effect of scale removing and disinfecting is achieved.



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## WATER TREATMENT METHOD AND DEVICE

### Field of the Invention

The present invention relates to water treating systems, particularly to scale removing and biocidal water treating systems.

### Background of the Invention

The problem of scale is inherent to all systems in which there is a flow of water that contains any of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  ions together with any of  $\text{OH}^-$ ,  $\text{CO}_3^{=}$ ,  $\text{HCO}_3^-$ ,  $\text{SiO}_3^{=}$ , or  $\text{SO}_4^{=}$ . Under certain temperature and pH conditions, carbonates, silicates, sulfates and hydroxide salts precipitate and cause blockage of nozzles, reduction of cross-section area of pipes, heat insulation and underdeposit corrosion. The well-known methods of removing scale from aqueous liquids are reverse osmosis and ion exchange. Another method for removing scale is direct current (DC) electrolysis. US 4,384,943 discloses a method of fluid treatment which comprises applying DC current to aqueous liquids.

Electrolytic treatment of aqueous fluids to produce biocides is well known in the art. For example, US 4,384,943 describes such a treatment which comprises maintaining in the fluid a compound that is electrochemically decomposable to yield bromine, chlorine or iodine and/or by decomposing water to produce biocidally active  $\text{O}_2$  or  $\text{O}_3$  oxidants.

US 5,424,032 describes a method of treating water using innocuous chemicals for the treatment of microorganisms, or employing ultraviolet light or electrolysis in order to destroy microorganisms.

The term "disinfecting", as used herein, means destroying various types of microorganisms to the extent that this prevents the formation of biological fouling, and disinfection of drinking water or of water for use in bathing.

Since scale removing and scale preventing are related processes, each of the terms "scale removing" and "scale preventing" herein mean both scale removing and scale preventing.

It is a purpose of the present invention to provide a process for preventing or at least inhibiting the growth of microorganisms in aqueous solutions, e.g., water, and for precipitating scale therefrom, which does not require the addition of chemicals to said solutions, and thus is an environmentally-friendly process. Thus, the invention solves many severe problems inherent to prior art methods. For instance, there are cooling systems in which the water is treated by the addition of chemicals. The bleed stream of such cooling systems cannot be used in many applications, due to the presence of said chemicals, and in many cases said bleed stream is wasted or requires expensive purification treatments to remove the chemicals, before it can be released into the environment.

It is another purpose of the present invention to provide a process for disinfecting aqueous liquids and for removing scale therefrom which permits to operate at a pH higher than 7, and even higher than 8.5.

It has now been found, and this is still another object of the invention, that in a system where a DC treatment having a combined effect of *in situ* production of biocides and of scale precipitation was applied to an aqueous fluid, e.g., pure water with no further additives, a dramatically lower percentage of scale was required to be precipitated than described in the prior art, in order to achieve substantially the same results of disinfecting and scale removing, as achieved for softened water described in the prior art.

### Summary of the Invention

The present invention provides a method of treatment of aqueous media, comprising applying to said aqueous medium in an electrolytic cell an electrical direct current of a magnitude and at a flow-rate of the liquid in said electrolytic cell such that a combined effect of scale removing and disinfecting is achieved.

The present invention further provides an aqueous fluid treatment device for scale removing and disinfecting comprising an electrolytic cell operated by a direct current source, said electrolytic cell being adapted to allow an aqueous medium to circulate therethrough.

The amount of direct current applied to said aqueous fluids varies according to the type of aqueous medium. For example, in the case of the treatment of cooling water, the preferred amount of direct current applied thereto is about  $1\text{ A}/5\text{ m}^3/\text{hour}$ .

Aqueous media that can be treated include, but are not limited to, drinking water, tap water, agriculture water, industrial water, sea water and sewage water. An advantage

of the present invention is that the pH at which it is possible to operate is not limited, so that it is possible to operate at a pH much higher than the prior art. As will be apparent to the skilled person, at pH of about 8-9 no corrosion inhibitors are required, because of the basic nature of the water, and this is another substantial advantage of the invention.

The device of the present invention can be used in any watering system, cooling system, heating system, water supplying system, and fogger. Said watering systems is can include, but are not limited to, drippers, sprinklers and foggers. Cooling systems include, e.g., cooling towers. Heating systems include, e.g., kettles, boilers, washing machines, dishwashers, quick water heaters, evaporators, radiators, steam generators, steam irons, steam cleaners, module water heaters, heating boosters, thermal convectors, greenhouse heaters, and central heating systems. Heating systems may further include, e.g., showers, sinks, bidets, bathtubs, hot tubs such as Jacuzzi-type tubs and whirlpools, spas and swimming pools.

Optionally, the aqueous medium can further be filtered, and thus the device of the present invention optionally further comprises, in case said device includes a liquid outlet, a filter connected to said outlet, through which the electrically treated aqueous fluid is driven.

#### **Brief Description of the Drawing**

- Fig. 1 schematically shows a water treatment device according to a preferred embodiment of the invention.

### Detailed Description of Preferred Embodiments

The present invention provides a method of treating aqueous solutions, which achieves a combined effect of scale removing and disinfecting. Such a method can meet the need of many systems in which both effects are required, such as agricultural systems in which water is distributed through narrow nozzles of sprinklers, drippers and foggers, and even a small quantity of scale and/or biofilm is liable to cause a blockage of said nozzles.

A treatment according to the present invention can be carried out, e.g., by a unit which comprises a liquid container having at least one liquid inlet and one liquid outlet, e.g., a pipe, further comprising at least one cathode and one anode placed within said liquid container, said cathode and anode being in electrical contact with the "-" and "+" poles of a direct current source, respectively. Said liquid inlet is connected to a water source, and said liquid outlet is connected to a target system, e.g., sprinklers, drippers and foggers, in which the disinfected, scale removed water is desired.

Furthermore, as stated above, the present invention is suitable for disinfecting liquids and for removing scale therefrom, in systems in which it is required to maintain a pH in the range 7 - 10. In the process of the invention, the pH changes only locally, near the electrodes, whereas in other systems, in which chemicals are added, the pH changes homogeneously, and may cause severe operational problems, such as corrosion.

As will be further discussed hereinafter, when the invention is applied to the treatment of cooling water no chemicals are added and therefore the bleed stream can be used in a wide range of applications, e.g., crops watering. Furthermore, as will be further illustrated in the examples to follow, the invention permits to employ water having a conductivity of 3,000  $\mu\text{S}$  or higher, up to about 6,000  $\mu\text{S}$ , without causing any substantial increase in corrosion. A typical pH for operating under these conditions is  $\text{pH} \approx 9$ . In this specification " $\mu\text{S}$ " indicates the  $\mu\text{Siemens}$  unit (which equals  $\mu\Omega^{-1}$ ). This result is both unexpected and remarkable, particularly since current standards, in cooling towers employing chemicals, is not greater than 3,000  $\mu\text{S}$ , and often as low as 2,000  $\mu\text{S}$ . The ability of allowing high conductivities, while preventing biofouling and scale formation, practically means that a smaller bleed – and consequently a smaller make-up of water – is needed in the operation of the cooling tower. Thus, when operating according to the invention, a reduction of up to about 30% in the make-up can be achieved, as well as a reduction of up to about 60% of the bleed, thus leading to a substantial saving in water usage and waste disposal.

The present invention can be carried out by means of any electrolytic cell. An example of such a cell is described, e.g., in Whitten et al., "General Chemistry with Qualitative Analysis", *Saunders College Publishing*, 4th ed., pp. 12-13.

It should be understood that the two processes that take place simultaneously (biocidal effect and scale prevention or removal) each require different, sometime contrasting operating conditions. Thus, in order to obtain a biocidal effect it is required to operate with high currents (the production rate of biocidal species in the



water is a function of the current) and high water flow-rates. On the other hand, in order to achieve a substantial anti-scale effect low water flow-rates are needed, while the magnitude of the current is of no consequence. It should further be noted that pH and precipitation conditions are much more severe at the electrodes than on the surfaces of the water apparatus.

Accordingly, preferred illustrative – but non-limitative – operating conditions are as follows:

The current required to obtain a substantial biocidal effect depends on the type of water treated and on the oxidant demand of the water. This can be estimated as:

$$1 \text{ A} = 1 \text{ gr O}_x/\text{hr}$$

wherein  $\text{O}_x$  is a  $\text{gr}_{(\text{eq})}$  of a monoelectronic oxidant such as  $\text{Cl}^*$ ,  $\text{OH}^*$ ,  $\frac{1}{2}\text{O}^*$  or  $\text{Br}^*$ .

In order to obtain a substantial biocidal effect in a typical water, it is required to provide a detectable residual amount – e.g., about 0.05 ppm, of active chlorine equivalent. The active chlorine equivalent present in the water can be determined using conventional methods, e.g., using the Chlor-Test kit manufactured by Merck KgaA, Germany, or the Lovibond kit manufactured by The Tintometer Ltd., UK, or by any other suitable method.

In order to obtain a substantial anti-scale effect, the linear flow velocity of water in the electrolytic cell (calculated as the flow rate divided by the cross section of the cell) should not exceed 500 m/hr, and should preferably be 100 m/hr or lower.

According to a particular embodiment, the invention is exploited in a Jacuzzi-type (whirlpool) hot tub or spa. In such environments there is a further important parameter, which is the turbidity of the water. A normal turbidity for clear water should not exceed 0.8 NTU (normal turbidity units). According to a preferred embodiment of the invention a whirlpool bath should operate with a current density of at least  $1 \text{ A/m}^2$ , in order to achieve normal turbidity and at the same time to avoid scaling effects and biofouling.

A water treatment device according to the present invention can be in a form such as that illustrated in Fig. 1, in which numeral 1 is a pipe, numeral 2 is a rectangular anode, and 3 and 4 each are rectangular cathodes (cathode boards). Anode 2 is positioned along the longitudinal axis of pipe 1. Cathode boards 3 and 4 are positioned along the longitudinal axis of pipe 1, one on each side of anode board 2 and both cathodes face anode 2. According to an alternative embodiment of the invention (not shown in the figure), pipe 1, made of metallic material may, by itself, function as the cathode, instead of cathodes 3 and 4, or in addition.

In the examples to follow a device essentially as described in Fig. 1 was employed, having the following dimensions: pipe 1 was a plastic pipe 60 inches long and having a diameter of 10 inches, the anode was a rectangular board made of titanium, coated with a catalytic coating and the two cathodes were each rectangular boards made of

steel. All three electrodes were each 50 inches long and 5 inches wide. The distance between each of the cathodes and the anode was 3 inches. Of course, the above dimensions will vary in different arrangements and shapes of the device, and they are provided herein for the purpose of exemplification only, and are in no way meant to limit the invention.

#### **Example 1 (comparative)**

A stream of non-treated water was used in a fog-generator used in a greenhouse, in which tomatoes were cultivated, for the purpose of cooling and keeping the temperature at a fixed level of about 25-30°C. Due to the precipitation of scale and the growth of microorganisms and algae around the nozzle, a blockage occurred at the nozzle and the nozzles had to be replaced. The average lifetime of nozzles in such system was 3 to 4 days.

#### **Example 2 (comparative)**

A stream of water treated by reverse osmosis was used in the same system as in Example 1. The average lifetime of the nozzles, in this case, was 1 to 2 months.

#### **Example 3**

A stream of water treated by DC current according to the present invention was used in the same system as that of Example 1. After three months there were no blockages registered in any of the approximately 1000 nozzles, and the upkeep of said nozzles was spared. Due to the use of the direct current treatment device of the invention, the water was disinfected and scale was removed therefrom to the extent that the

problem of blockages was solved for all practical purposes. Furthermore, the water was free from chemical additives and was suitable for a wide range of uses. Tomatoes that were watered with the treated water showed no decay of growth. These results show a substantial improvement over the systems of Examples 1 and 2.

#### **Example 4 (comparative)**

A stream of non-treated water was used in a cooling tower operating at a flow rate of 500 m<sup>3</sup>/hr, with a make-up of 30 m<sup>3</sup>/hr, and a bleed of 10 m<sup>3</sup>/hr. The conductivity of the tap water was about 1,000  $\mu$ S, and that of the bleed stream (and, hence, of the recirculating water) was 3,000  $\mu$ S. After two weeks, a substantial layer of biofilm and scale was observed on the walls of the tower. The water in the tower was turbid.

#### **Example 5 (comparative)**

A stream of water treated by polyphosphonates, sulfuric acid and corrosion inhibitors at a pH of less than 8 was used in the cooling tower of Example 4. As a result, the pH was unstable and scale and biofilm appeared on the walls of the tower, and were removed every three months in order to allow a smooth functioning of the tower. Metallic elements showed some corrosion. The water in the tower was turbid, and was not suitable for watering processes.

#### **Example 6**

A stream of water of with a recirculation stream of 50 m<sup>3</sup>/hr treated by DC current according to the present invention was used in the system of Example 4 at the time that a layer of biofilm, as well as scale, were already present. The conductivity of the

bleed stream was 5,000  $\mu\text{S}$ . The pH was 8.8. The make-up was 20  $\text{m}^3/\text{hr}$  and the bleed 4  $\text{m}^3/\text{hr}$ . After two weeks, said layer disappeared, and the water in the tower was clear. No corrosion was noted. The bleed flow was of a quality suitable for watering processes. Due to the use of the direct current treatment device of the invention, the water was disinfected to the extent that not only did further biofilm not appear on the walls of the tower, but the existing biofilm vanished. The clear water, scale and biofilm removal, and the "green" use of the bleed flow of the present example show a substantial improvement over the results of Examples 4 and 5.

#### Example 7

A 2  $\text{m}^3$  Jacuzzi-type hot-tub was used for this example. The turbidity in the water was 0.5 NTU. The whirlpool was operated for 4 consecutive hours with 4 persons bathing each during 1 hour, without the addition of any chemicals. The turbidity at the end of this 4-hour period was 3 NTU. The whirlpool was then operated empty, together with an electrolytic cell treating water with a maximal recycle ratio of 6/hr (number of volumes recirculated per hour), at 10A for 2 hours, at the end of which period the turbidity was 0.1 NTU. The redox potential was 600 mV. The make-up of water to the tub was effected on demand by a level indicator that controlled the level of water in the tub.

The experiment was repeated daily during two weeks, without any water replacement, and the turbidity dropped each time to the same value of 0.1 NTU.

Additionally, the redox potential of the water was measured about 3 hours after the bathing, and was found consistently to be in the range 500 – 700 mV, with a detectable amount of oxidants. Furthermore, during this experiment 150 gr of scale were removed from 2 m<sup>3</sup> of water, containing mainly CaCO<sub>3</sub> and Mg(OH)<sub>2</sub>.

A comparative test was also run with currents below 2A, and it was found that below this value it was not possible to reach a redox potential greater than 500 mV. The turbidity of the water, however, still remained at a suitable level (0.1 NTU).

As will be apparent to the skilled person, the above results are greatly advantageous for use in bathing systems, such as whirlpool. It should further be noted that the control of the turbidity is of great importance, since it is undesirable to replace the water in the whirlpool, because fresh water carries with it added amounts of carbonates which cause the clogging of orifices.

The above description and examples have been provided for illustrative purposes only, and are not intended to limit the invention in any way. It will be apparent to the skilled person that many modifications, variations and adaptations may be made to the invention by persons skilled in the art, without departing from the spirit of the invention or exceeding the scope of the claims.

CLAIMS:

1. A method of treatment of aqueous media comprising applying to said aqueous medium in an electrolytic cell an electrical direct current of a magnitude and at a flow-rate of the liquid in said electrolytic cell such that a combined effect of scale removing and disinfecting is achieved.
2. A method according to claim 1, wherein the current is such as to generate detectable residual amount of active chlorine equivalent in the water.
3. A method according to claim 2, wherein the residual amount of active chlorine equivalent in the water is 0.05 ppm or higher.
4. A method according to any one of claims 1 to 3, wherein the linear flow-rate of aqueous medium through the electrolytic cell is 500 m/hr or less, preferably 100 m/hr or less.
5. A method according to any one of claims 1 to 4, wherein the aqueous medium is water from a whirlpool, the current density is at least  $1 \text{ A/m}^3$ .
6. A method according to any one of claims 1 to 4, wherein the aqueous medium is water from a cooling tower, and the conductivity in the recirculating water is between  $3,000 \text{ }\mu\text{S}$  and  $6,000 \text{ }\mu\text{S}$ .

7. A method according to any one of claims 1 to 4, wherein the aqueous medium is selected from a group which consists of tap water, agricultural water, industrial water, sea water and sewage water.
8. A method according to any one of claims 1 to 7, wherein the pH of the water is maintained at a value above 7.
9. A method according to claim 8, wherein the pH is in the range 8 – 9.
10. An aqueous fluid treatment device for scale removing and disinfecting comprising an electrolytic cell operated by a direct current source, said electrolytic cell being adapted to allow an aqueous medium to circulate therethrough.
11. An aqueous fluid treatment device according to claim 8, for use in agriculture watering systems.
12. A device according to claim 11 wherein the watering systems are selected from the group which consists of drippers, sprinklers and foggers.
13. An aqueous medium treatment device according to claim 10, for use in a cooling system.
14. A device according to claim 13, wherein said cooling system is a cooling tower.



15. An aqueous medium treatment device according to claim 10, for use in a heating system.

16. A device according to claim 15, wherein said heating system is selected from the group consisting of kettles, boilers, washing machines, dishwashers, quick water heaters, evaporators, radiators, steam generators, steam irons, steam cleaners, module water heaters, heating boosters, thermal convectors, greenhouse heaters, and central heating systems.

17. An aqueous medium treatment device according to claim 10, for use in a water supplying system.

18. A device according to claim 15, wherein said heating system is selected from the group that consists of showers, sinks, bidets, bathtubs, hot tubs, particularly Jacuzzi-type tubs and whirlpools, spas and swimming pools.

19. An aqueous medium treatment device according to claim 10, for use in a fogger.

20. A cooling tower system comprising:

- a cooling tower; and
- a device according to claim 10;

said cooling tower being adapted to bleed water and to receive make-up water when the conductivity of said water is in the range 3,000  $\mu$ S – 6,000  $\mu$ S.



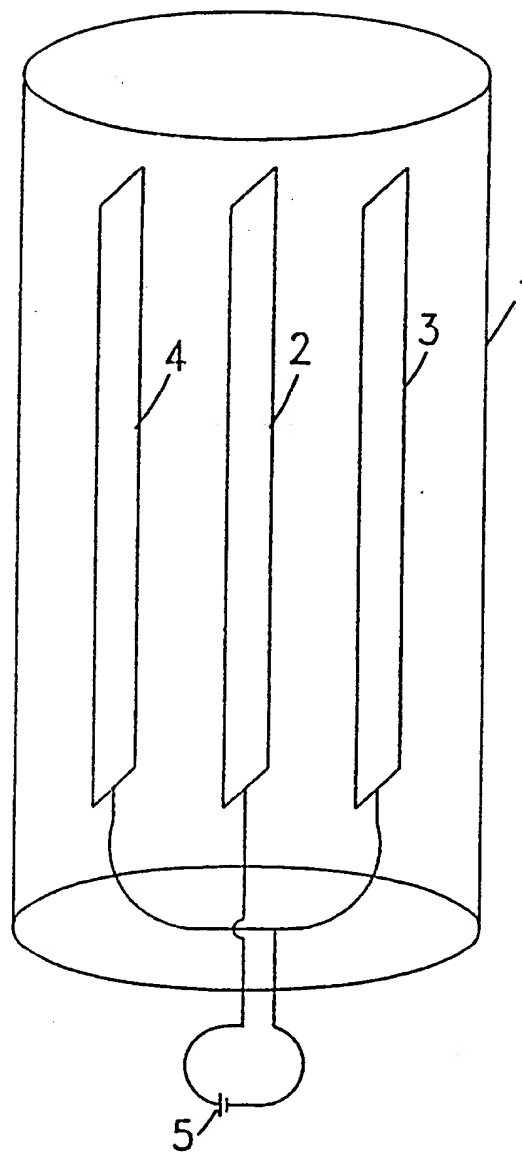


Fig. 1

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/IL 98/00453

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C02F1/46

According to International Patent Classification (IPC) or to both national classification and IPC

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IPC 6 C02F

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 4 048 030 A (MILLER JORGE) 13 September 1977 see column 2, line 21 - column 8, line 68	1-3,7, 10,16-18 4-6,8,9, 11-15, 19,20
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X A	US 5 389 210 A (SILVERI MICHAEL A) 14 February 1995 see column 2, line 35 - column 4, line 11	1,9,10, 17,18 2-9, 11-16, 19,20

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Date of the actual completion of the international search

19 January 1999

Date of mailing of the international search report

27/01/1999

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# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X A	US 5 580 438 A (SILVERI MICHAEL A) 3 December 1996 see column 2, line 66 - column 4, line 3	1, 10, 18 2-9, 11-17, 19, 20
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